



CENG 6405: Pollutant Fate and Transport

1. Pollutant is identified
2. Its source is identified
3. Its temporal and spatial distribution is estimated
4. Risk assessment will be conducted
5. Decision or plan of remediation is negotiated



CENG 6405: Pollutant Fate and Transport

Chapter 1: Introduction to pollutant fate and transport

1. Sources and types of pollutant
2. An overview of pollutant fate and transport modeling
 1. The mass balance and representative elementary volume
 2. Pollutant transport mechanisms
 3. Physical, Chemical, and Biological Transformations
 4. Chemical distribution among phases

Definitions

- **Chemical Transport** - Processes that move chemicals through environmental media.
- **Chemical Fate** - The eventual disposition of a chemical contaminant. This can include destruction or long term storage in a sink and/or exposure-biotransformation in ecological and human receptors.
- Environmental Media: **Air, Surface Water, Sediment, Groundwater - Saturated Zone, Soil - Top soils, Subsurface area - Vadose Zone - Unsaturated Zone**

Definition ...

- When **Harmful Substances Contaminate the environment** it is Called Pollution.
- Pollution can be defined as any undesirable change in the physical, chemical, biological characteristics of any component of **the environment which can cause harm to life and property.**
- **What is the difference between a pollutant and a contaminant?**

Why study the fate and transport of pollutants?

- Do not respect media boundaries or political boundaries.
- Modeling transport within one medium will not completely describe the chemicals fate.
- Predictive capability of the movement of chemicals for both
 - Environmental monitoring and validation and
 - Development of engineering, institutional and/or administrative controls.

Chemical Concentration

- The chemical concentration is the measure of the mass of a chemical in a specific volume or mass of air, water, soil etc.
- **Units of concentration in Water:**
 - Mass of chemical per unit volume of water [M/L^3].
 - Molarity, M, Normality (N)
 - Ppm by volume { ppm (v) }. 1 ppm = 1 mg of chemical/liter of water.

Chemical Concentration

■ Units of concentration in Soil:

- Expressed in mass of chemical per unit volume of soil

[M/L³] (??)

- Ppm (w) = mg of chemical/kg soil and ppb is microgram of chemical/kg soil.

■ Units of concentration in Air:

- Expressed in mass of chemical per unit volume of Air

[M/L³] (??)

- ppm (v), So 1 ppm of helium in air is 1ml Helium per 1000 liters (1 m³) air.

1.1 Sources and types of pollutant

- **Point sources** are direct discharges to a single point;
 - Examples include discharges from sewage treatment plants, injection wells and some industrial sources.
- **Non-point sources** are diffused across a broad area and their contamination cannot be traced to a single discharge point.
 - Examples agricultural lands & residential areas; urban runoff & energy production; and sediment from improperly managed construction sites & eroding stream banks.

Air Pollution

Sources

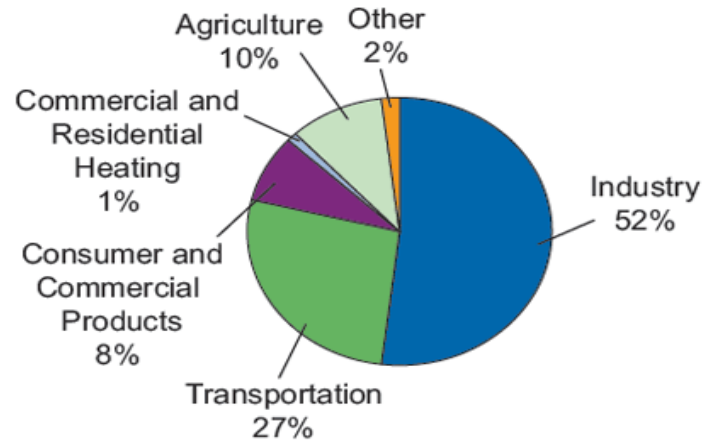
Natural

Volcanic Eruptions, Forest Fires, Sea Salt Sprays, Biological Decay, Pollen Grains, Marshes

Anthropogenic

Thermal Power Plants, Vehicular Emissions, Industrial Units

Sources of Emissions of Air Pollutants



Surface Water Pollution: Domestic Sewage

- Refers to waste water that is discarded from households. Also referred to as sanitary sewage, such water contains a wide variety of dissolved and suspended impurities.
- It is large by volume and contains impurities such as organic materials and plant nutrients that tend to rot.
- The main organic materials are food and vegetable waste, plant nutrient come from chemical soaps, washing powders, etc.
- Domestic sewage is also very likely to contain **disease-causing microbes.**

Surface Water Pollution: Industrial Effluents

- Waste water from manufacturing or chemical processes in industries
- Industrial waste water usually contains specific and readily identifiable chemical compounds.
- Mainly in the form of toxic wastes and organic pollutants.
- Chromium, mercury, lead, copper, cadmium etc

Surface Water Pollution: Synthetic Detergents

- Added because of washing clothes, cleaning utensils.
- In industries for washing
- Add surfactants and soaps to water
- Toxic to fish, aquatic life.

Surface Water Pollution: Agricultural Run Off

- Routine applications of fertilizers and pesticides for agriculture and uncontrolled run off in water bodies.
- Adds Nitrogen and Phosphorus to water
- Causes Eutrophication and algal blooms.



Groundwater Pollution

- Septic tanks
- Mining
- Deep well injection
- Arsenic, Nitrate, Fluoride
- Irrigation/agriculture
- Is less comparatively as soil acts as a filter but difficult to remediate

Thermal Pollution

- Definition : Presence of waste heat in the water/air which can cause undesirable changes in natural environment.
- Causes:
 - Heat producing Industries
 - Power plants utilize only $1/3^{\text{rd}}$ energy produced by fossil fuel the rest is wasted as heat
 - Cold water is taken from water body for coolingused and left in the water body....back with increase of $10 - 15^{\circ}\text{C}$

Effects of thermal pollution

- Oxygen penetration decreases, DO reduces as the solubility decreases
- Metabolic Activities increase requiring more oxygen.
- Heat kills fishes and other aquatic life.
- Toxicity of pesticides & chemicals increase
- Spawning is disturbed
- Fish migration is affected
- Composition of flora & fauna changes

1.2 Overview of fate and transport modeling

- For a particular chemical present at a specific location at a certain time there are three possible outcomes
 - The chemical can remain in that location and/or
 - The chemical can be transported elsewhere and/or
 - The chemical can be transformed into another chemical.
- By accounting for material entering and leaving a system, mass flows can be identified which might have been unknown, or difficult to measure without this technique.

Mass Balance

- The water balance equation (conservation of mass) has Two common ways to write

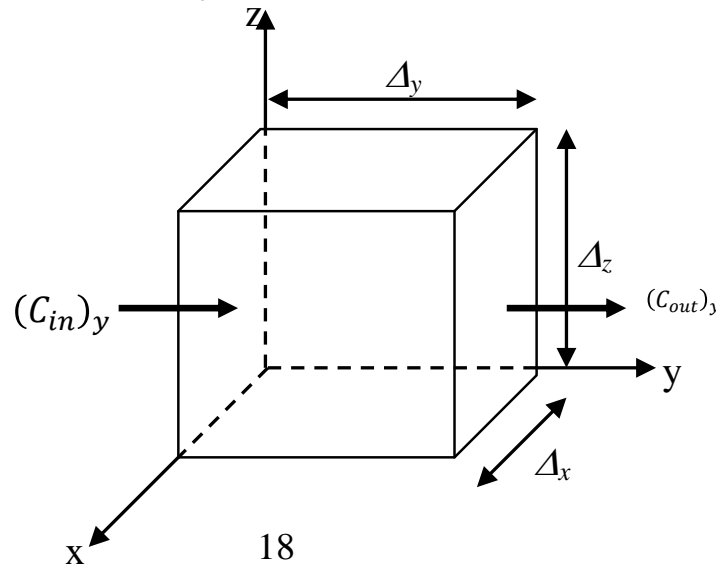
1. Mass in – Mass out = Change in mass

$$(C_{in} - C_{out})_x + (C_{in} - C_{out})_y + (C_{in} - C_{out})_z = \Delta C; C_{in} \text{ mass unit}$$

2. Mass inflow – Mass outflow = Rate of change in mass

$$(C_{in} - C_{out})_x \Delta y \Delta z + (C_{in} - C_{out})_y \Delta x \Delta z + (C_{in} - C_{out})_z \Delta x \Delta y = \Delta C$$

C_{in} mass per unit time



Mass Balance Expression

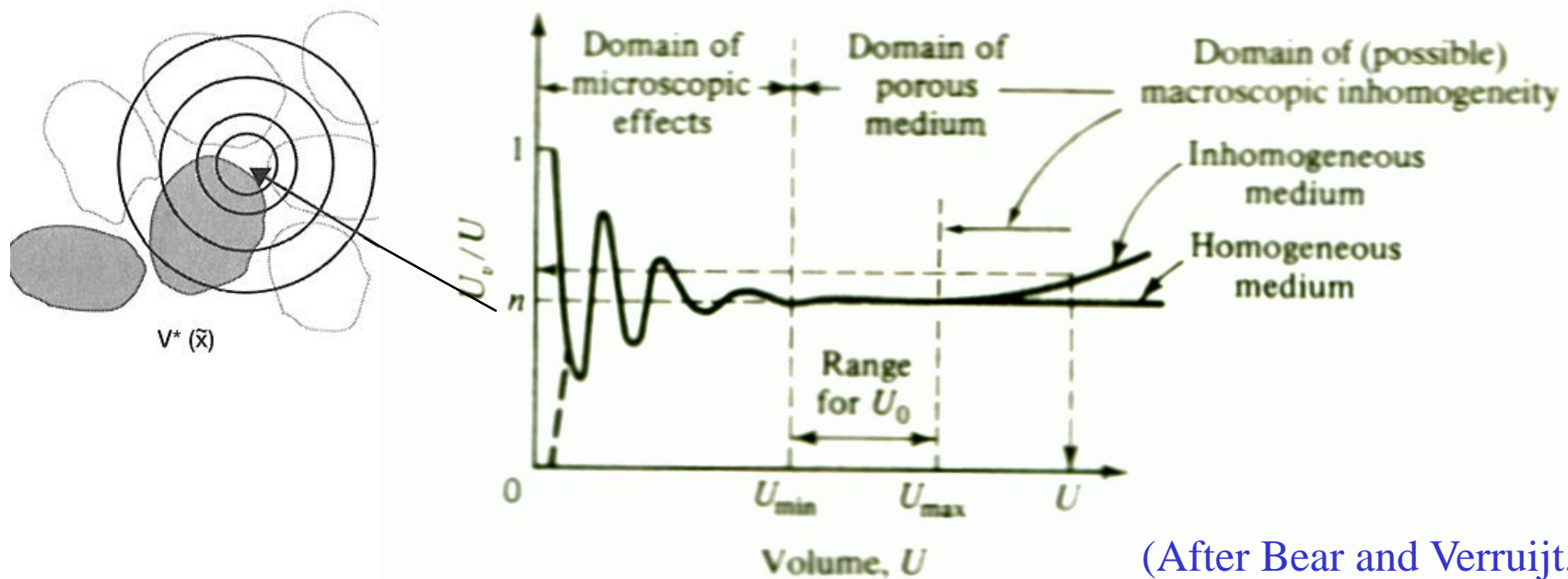
- Mass transported_{in} - Mass transported_{out} + Mass produced_{by sources} - Mass consumed_{by sinks} = Δ_{storage} mass in control volume
- $[M/T]_{\text{in}} - [M/T]_{\text{out}} + [M/T]_{\text{sources}} - [M/T]_{\text{sinks}} =$

Rate of Δ_{in} mass in the storage

- If all but one of the terms are known, or can be estimated, then the mass balance expression can be rearranged to determine an otherwise unmeasurable transport, source or sink term.
- Steady state situations result in a net storage of 0 (Δ_{in} mass in the storage = 0).

Concept of REV: Continuum assumption

- Any property of a medium taken over a suitably selected volume is generally called representative elementary volume (REV).

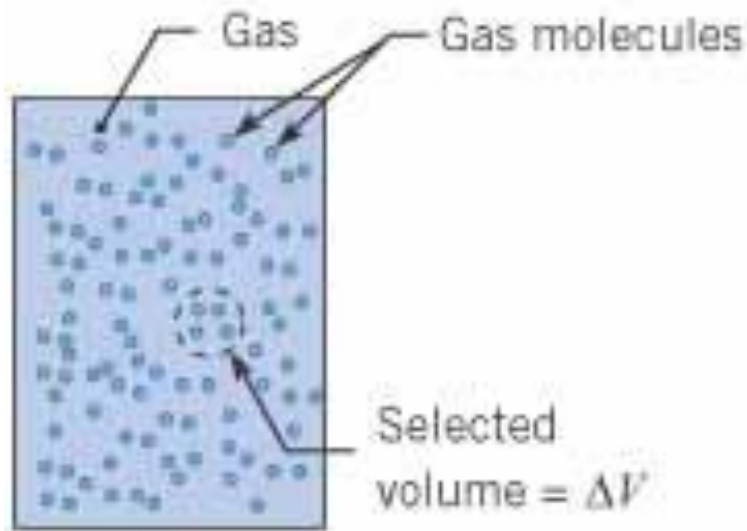


(After Bear and Verruijt, 1987)

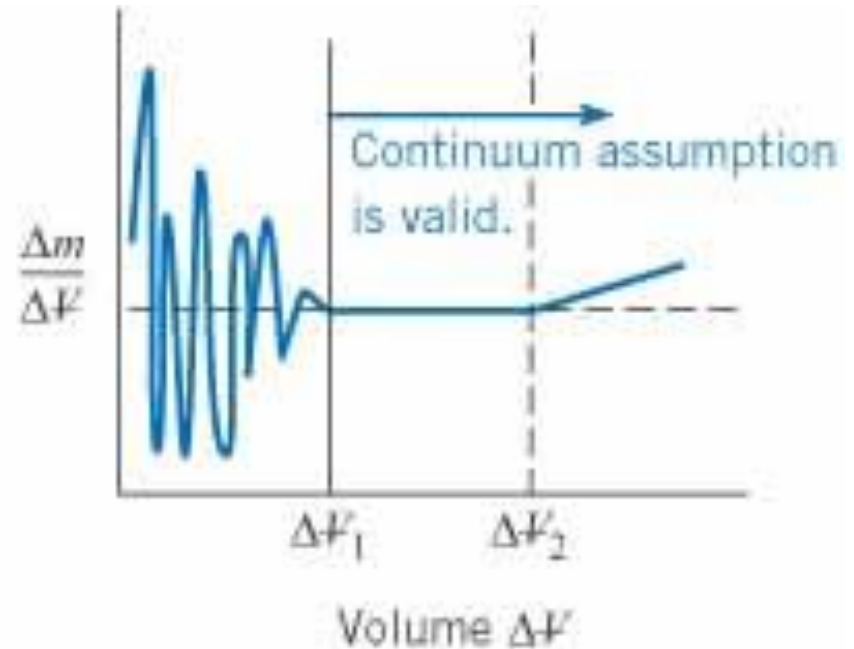
Concept of REV: Dimension and physical meaning porous medium

Concept of REV: Continuum assumption

- Concept of REV: Dimension and physical meaning fluid medium



(a)



(b)

Source: Engineering Fluid Mechanics

Pollutant transport mechanisms

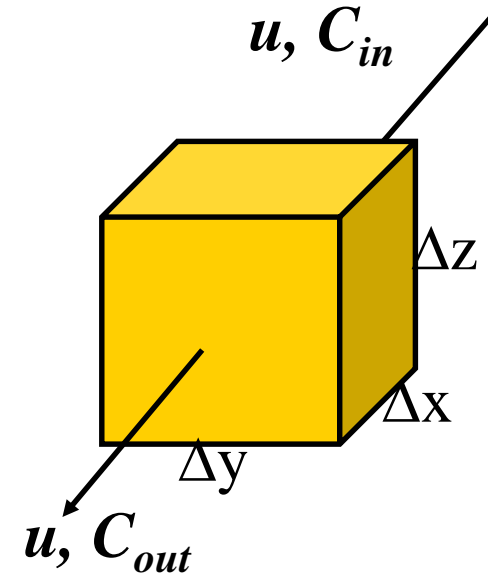
- Depending on the level of mixing, fluid transport of contaminants (pollutants) can be transported by:
 - Advection
 - Molecular Diffusion
 - Turbulent Diffusion
 - Shear Flow Dispersion

Advection

- Advection is **movement of the contaminant with the fluid.**
- Consider a conservative material, in the absence of any diffusive mechanisms, moving in one direction.
- The absence of any diffusive activity means that the pollutant remains associated with the same water “packet” with which it was initially associated.
- The mass balance on representative elementary volume (REV):
 - $\text{Mass flow}_{\text{in}} - \text{Mass flow}_{\text{out}} = \text{time rate of accumulation in REV.}$

Advection

- Let $Q = \text{flow rate} = U(\Delta z \Delta y)$.
- Where $U = \text{fluid flux (m/sec)}$.



- Then

$$\begin{aligned} Q_{in}C_{in} - Q_{out}C_{out} &= \frac{\Delta C_{vol}}{\Delta t} \Delta x \Delta y \Delta z \\ \Rightarrow \frac{(Q_{in}C_{in} - Q_{out}C_{out})}{\Delta x \Delta y \Delta z} &= \frac{\Delta C_{vol}}{\Delta t}, \text{ Note } u = \frac{Q}{\Delta y \Delta z} \\ \Rightarrow \frac{\Delta(uC)}{\Delta x} &= -\frac{\Delta C_{vol}}{\Delta t}, \text{ where } \Delta C_{vol} = C_{out} - C_{in} \end{aligned}$$

Advection

- In the limit, the size of **the elemental volume become REV**
and the change in time infinitely small :

$$\blacksquare - \frac{\partial C}{\partial t} = \frac{\partial(uC)}{\partial x}$$

- In three dimensions

$$\blacksquare - \frac{\partial C}{\partial t} = \frac{\partial(uC)}{\partial x} + \frac{\partial(vC)}{\partial y} + \frac{\partial(wC)}{\partial z}$$

- Where u , v and w are the velocity vectors in x -, y - and z -
directions

Solution to 1 D Advective transport with **steady uniform velocity**

$$\blacksquare \frac{\partial C}{\partial t} = - \frac{\partial(uC)}{\partial x} \Rightarrow \frac{\partial C}{\partial t} + u \frac{\partial C}{\partial x} = 0$$

- IDEA: Perform a linear change of variables to eliminate one partial derivative:

$$\blacksquare \alpha = ax + bt,$$

$$\blacksquare \beta = cx + dt,$$

- where:

- x, t : original Independent variables,

- α, β : new independent variables,

- a, b, c, d : constants to be chosen “**conveniently**,” but must satisfy: $ad - bc \neq 0$.

- We use the multivariable chain rule to convert to α and β derivatives:

$$\begin{aligned} \blacksquare \frac{\partial C}{\partial t} &= \frac{\partial C}{\partial \alpha} \frac{\partial \alpha}{\partial t} + \frac{\partial C}{\partial \beta} \frac{\partial \beta}{\partial t} = b \frac{\partial C}{\partial \alpha} + d \frac{\partial C}{\partial \beta}; \quad \frac{\partial C}{\partial x} = \frac{\partial C}{\partial \alpha} \frac{\partial \alpha}{\partial x} + \frac{\partial C}{\partial \beta} \frac{\partial \beta}{\partial x} = \\ &a \frac{\partial C}{\partial \alpha} + c \frac{\partial C}{\partial \beta}; \end{aligned}$$

$$\begin{aligned} \blacksquare \frac{\partial C}{\partial t} + u \frac{\partial C}{\partial x} &= \left(b \frac{\partial C}{\partial \alpha} + d \frac{\partial C}{\partial \beta} \right) + u \left(a \frac{\partial C}{\partial \alpha} + c \frac{\partial C}{\partial \beta} \right) \Rightarrow (b + \\ &au) \frac{\partial C}{\partial \alpha} + (d + cu) \frac{\partial C}{\partial \beta} = 0 \end{aligned}$$

- Choosing $a = 0$, $b = 1$, $c = 1$, $d = -u$, the original PDE becomes

$$\blacksquare \frac{\partial C}{\partial \alpha} = 0 \Rightarrow C = f(\beta) = f(x - ut)$$

- where f is any differentiable function of one variable.

Example:

- A water in open canal moves with uniform velocity of 3 m/s. the initial concentration distribution of the chemical is given by:

$$C(x, 0) = xe^{-x^2}$$

- What is the concentration profile in the open channel?

- Solve the eqn. $\frac{\partial C}{\partial t} + 3 \frac{\partial C}{\partial x} = 0$

- We know that the general solution is: $C(x, t) = f(x - 3t)$

- To find f we use the initial condition: $f(x) = f(x - 3 \times 0) =$

$$C(x, 0) = xe^{-x^2} \Rightarrow C(x, t) = (x - 3t)e^{-(x-3t)^2}$$

Practice exercise 1

- A water in open channel moves with velocity of $u = (3xt)$ m/s. the initial concentration distribution of the chemical is given by: $C(x, 0) = xe^{-x^2}$
- What is the concentration distribution in the open channel?
- Hint:
- Note that u varies with both time and space
- Start solving it from

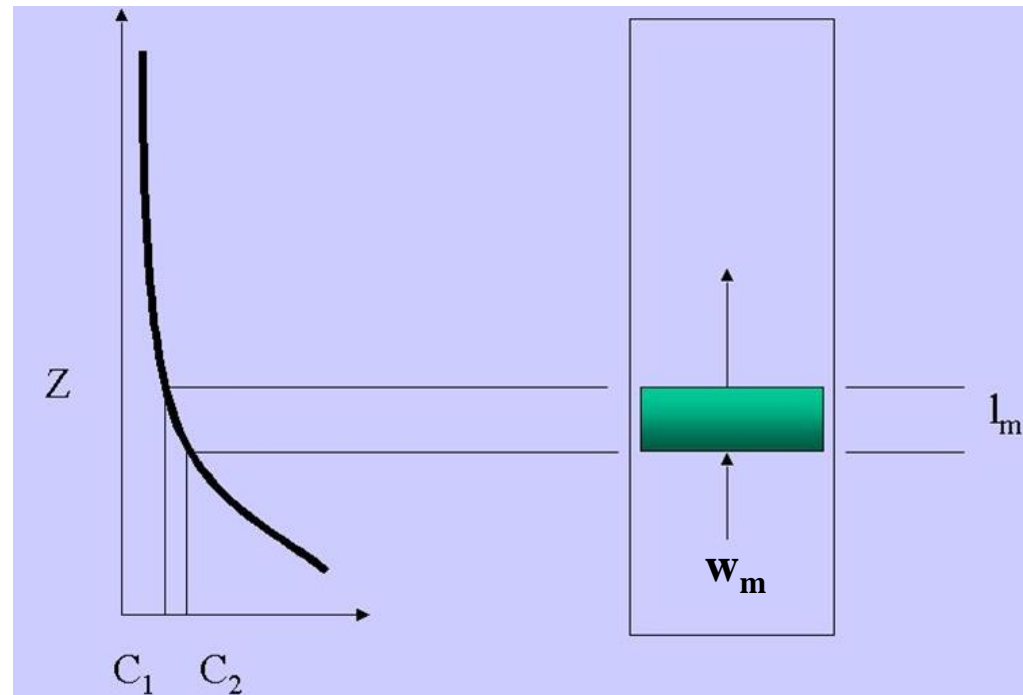
$$\blacksquare \frac{\partial C}{\partial t} = - \frac{\partial(uC)}{\partial x}$$

Molecular diffusion

- Molecular diffusion is a phenomenon caused by kinetic energy of molecules and by concentration gradients. Molecules undergo random motion caused by their internal energy.
- Each molecule possesses at least three types of energy: **(i) Translational (only significant in the diffusion process), (ii) Rotational AND (iii) Vibration-al**
- Commonly molecular diffusion is overwhelmed by turbulence. But at interfaces (water - air and water - solid) molecular diffusion can become important.

Mathematical Model (Fick's Law)

- Consider the situation where a concentration gradient exists (by some set of initial conditions).
- Let molecules move at velocity of w_m (in the z direction).
- Define l_m as the average distance particles travel before they collide with other particles. l_m is called the **mean free path**



Mathematical Model (Fick's Law)

- The net mass flux into the shaded region is given by (on a unit area basis):

- $J_z = C_{in}w_m - C_{out}w_m = w_m(C_{in} - C_{out})$

- J_z (flux) has typical units of mass/(m².sec)

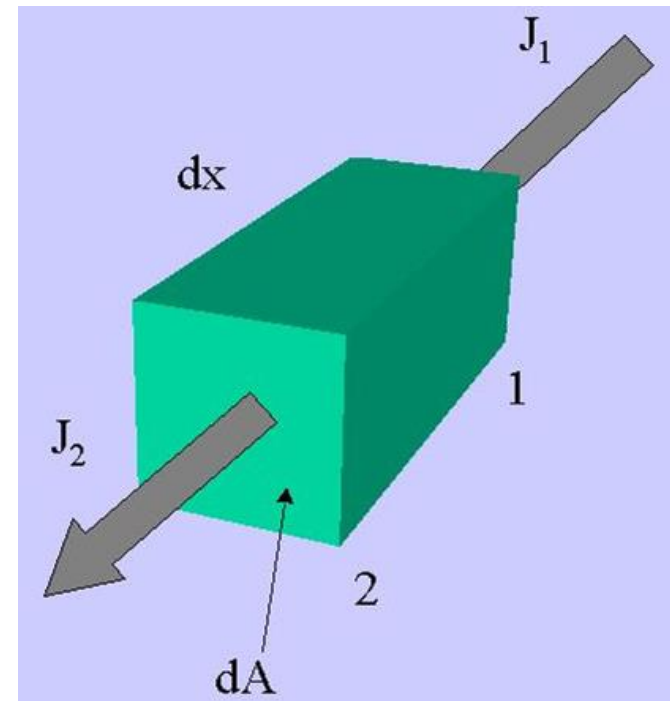
- If the distance and concentration are small enough:

- $\frac{C_{out} - C_{in}}{l_m} \approx \frac{\partial C}{\partial z} \Rightarrow C_{in} - C_{out} = -l_m \frac{\partial C}{\partial z} \Rightarrow J_z = -w_m l_m \frac{\partial C}{\partial z}$

- The product $w_m l_m = D_z$ (**coefficient of molecular diffusivity**). D_z has typical units of cm²/ sec.
- $D_{x/y/z}$ is a function of temperature, solvent & molecule type and size.
- In three dimensions: $-J = D_x \frac{\partial C}{\partial x} + D_y \frac{\partial C}{\partial y} + D_z \frac{\partial C}{\partial z}$ **(Fick's Law)**

Molecular diffusion

- Now look at transport with just molecular diffusion, i.e., assume no advection. Again a mass balance can be performed on an elemental volume for a conservative material.
- Again assume that diffusion occurs in the x-direction only (both positive and negative).
- $J_1 = -D_x \left(\frac{\partial C}{\partial x} \right)_1$ and
- $J_2 = -D_x \left(\frac{\partial C}{\partial x} \right)_2$



- Again using in – out = mass rate of accumulation in the REV gives:

- $$dA \left\{ -D_x \left(\frac{\partial C}{\partial x} \right)_1 - \left[-D_x \left(\frac{\partial C}{\partial x} \right)_2 \right] \right\} = \frac{\partial M}{\partial t}$$

But
$$D_x \left(\frac{\partial C}{\partial x} \right)_2 = D_x \left(\frac{\partial C}{\partial x} \right)_1 + \frac{\partial}{\partial x} \left(D_x \frac{\partial C}{\partial x} \right) dx$$

$$\Rightarrow -\cancel{D_x \left(\frac{\partial C}{\partial x} \right)_1} + \cancel{D_x \left(\frac{\partial C}{\partial x} \right)_1} + \frac{\partial}{\partial x} \left(D_x \frac{\partial C}{\partial x} \right) dx = \frac{\partial M}{dA \partial t}$$

Dividing by dx

$$\frac{\partial}{\partial x} \left(D_x \frac{\partial C}{\partial x} \right) = \frac{\partial M}{dA dx \partial t} = \frac{\partial M}{dV \partial t} = \frac{\partial C}{\partial t}$$

Fick's second Law

- In three dimensions

- $$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D_x \frac{\partial C}{\partial x} \right) + \frac{\partial}{\partial y} \left(D_y \frac{\partial C}{\partial y} \right) + \frac{\partial}{\partial z} \left(D_z \frac{\partial C}{\partial z} \right)$$

Similarity solution One-dimensional diffusion equation

- A classic solution from Fischer et. al. (1979) give:

$$\blacksquare \frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right)$$

$$\blacksquare C(x, t) = \frac{M}{A\sqrt{4\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right)$$

- For 3D

$$\blacksquare C(x, y, z, t) = \frac{M}{4\pi t \sqrt{4\pi D_x D_y D_z t}} \exp\left(-\frac{x^2}{4D_x t} - \frac{y^2}{4D_y t} - \frac{z^2}{4D_z t}\right)$$

- where M is the total mass of substance injected.

One Dimensional equation Method of separation of variables Example:

- The ends A and B of a stagnant clean water pipe, 200 cm long, have concentration at 0 and 40 mg/cm³ until steady state prevails. If the concentration of the end B changed to 0. Find the concentration distribution in the pipe at any time t. Take D as 10⁻² cm²/s.

$$\frac{\partial C}{\partial t} = 0.01 \frac{\partial^2 C}{\partial x^2}$$

For Steady state

$$\frac{d^2 C}{dx^2} = 0, \quad \text{up on integration} \rightarrow C(x) = c_1 x + c_2$$

Up on substitution of BCs: $C(0) = 0$, $c_2 = 0$ and $C(200) = 40$ brings $c_1 = 0.2$

Since the concentration at B is suddenly changed we gain transient state whose initial condition could be described by $C(x) = 0.2x$

One Dimensional equation Method of separation of variables Example:

$$\frac{\partial C}{\partial t} = 0.01 \frac{\partial^2 C}{\partial x^2}$$

Let $C = TX$ is the solution, In which T is a function of t and X is a function of x only.

$$\frac{\partial C}{\partial t} = \frac{\partial(TX)}{\partial t} = X \frac{\partial T}{\partial t} + T \frac{\partial X}{\partial t} = X \frac{dT}{dt} = XT' \text{ and}$$

$$\frac{\partial C}{\partial x} = \frac{\partial(TX)}{\partial x} = X \frac{\partial T}{\partial x} + T \frac{\partial X}{\partial x} = T \frac{dX}{dx} = TX'$$

$$\frac{\partial^2 C}{\partial x^2} = \frac{\partial}{\partial x} \left(\frac{\partial C}{\partial x} \right) = \frac{\partial}{\partial x} (TX') = X' \frac{\partial T}{\partial x} + T \frac{\partial X'}{\partial x} = T \frac{dX'}{dx} = TX''$$

Substituting

$$X \frac{dT}{dt} = 0.01T \frac{d^2 X}{dx^2} \rightarrow \frac{dT}{Tdt} = 0.01 \frac{d^2 X}{Xdx^2} = \text{Constant}$$

$$\frac{dT}{Tdt} = -c^2 \text{ and } 0.01 \frac{d^2 X}{Xdx^2} = -c^2$$

From the first equation $\frac{dT}{T} = -c^2 dt \rightarrow T = c_1 e^{-c^2 t}$

One Dimensional equation Method of separation of variables Example:

$$0.01 \frac{d^2 X}{dx^2} = -c^2 \rightarrow \frac{d^2 X}{dx^2} + 100c^2 X = 0$$

Solving this ODE

$$X = c_2 \sin(10cx) + c_3 \cos(10cx)$$

Thus the $C = TX$, become

$$C(x, t) = c_1 e^{-c^2 t} (c_2 \sin(10cx) + c_3 \cos(10cx))$$

$$C(x, t) = e^{-c^2 t} (c_4 \sin(10cx) + c_5 \cos(10cx))$$

Where $c_4 = c_1 \times c_2$ and $c_5 = c_1 \times c_3$

Substituting the boundary conditions for transient situation

$$C(0, t) = 0 = e^{-c^2 t} (c_4 \sin(0) + c_5 \cos(0)) \rightarrow c_5 = 0$$

$$\rightarrow C(x, t) = e^{-c^2 t} (c_4 \sin(10cx))$$

$$C(200, t) = 0 = e^{-c^2 t} (c_4 \sin(2000c)) \rightarrow \sin(2000c) = 0 = \sin(n\pi)$$

$$\rightarrow c = \frac{n\pi}{2000} \rightarrow C(x, t) = \sum_{n=1}^{\infty} b_n e^{-\left(\frac{n\pi}{2000}\right)^2 t} \sin\left(\frac{n\pi x}{200}\right)$$

One Dimensional equation Method of separation of variables Example:

Substituting the initial condition

$$C(x, 0) = 0.2x = \sum_{n=1}^{\infty} b_n \sin\left(\frac{n\pi x}{200}\right)$$

This is half range Fourier sine series with period of 200

$$b_n = \frac{2}{200} \int_0^{200} 0.2x \sin\left(\frac{n\pi x}{200}\right) dx$$

$$b_n = \frac{2}{200} \left[0.2x \frac{200}{n\pi} \left(-\cos\left(\frac{n\pi x}{200}\right) \right) - \left(\frac{200}{n\pi}\right)^2 \sin\left(\frac{n\pi x}{200}\right) \right]_0^{200}$$

$$b_n = (-1)^{n+1} \frac{80}{n\pi}$$

$$C(x, t) = \sum_{n=1}^{\infty} \left((-1)^{n+1} \frac{80}{n\pi} \right) e^{-\left(\frac{n\pi}{200}\right)^2 t} \sin\left(\frac{n\pi x}{200}\right)$$

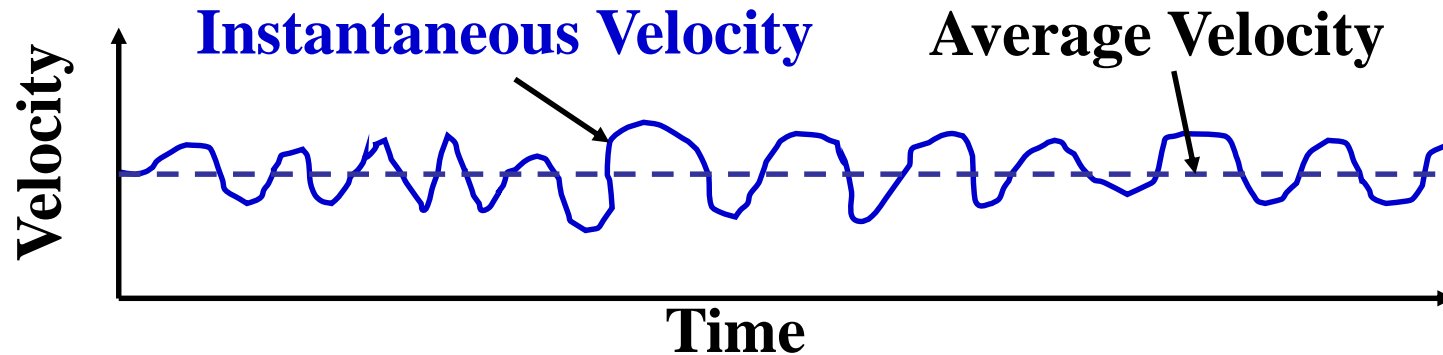
Advection Diffusion equation:

- Both advection and diffusion are usually active simultaneously and they are **linear processes**, therefore, their governing equations are additive yielding what's known as the advective-diffusion equation (ADE).

$$\frac{\partial C}{\partial t} + \left(\frac{\partial(uC)}{\partial x} + \frac{\partial(vC)}{\partial y} + \frac{\partial(wC)}{\partial z} \right) =$$
$$\frac{\partial}{\partial x} \left(D_x \frac{\partial C}{\partial x} \right) + \frac{\partial}{\partial y} \left(D_y \frac{\partial C}{\partial y} \right) + \frac{\partial}{\partial z} \left(D_z \frac{\partial C}{\partial z} \right)$$

Turbulent Diffusion

- Basically turbulent diffusion is due to random fluctuation in advective velocity.



- It's very difficult to mathematically describe instantaneous velocity since it has a **random component (u')**. Instantaneous velocity (u) has two components (**Reynolds decomposition**):
 - $u = \bar{u} + u'$ where $\int u' dt = 0$
 - where \bar{u} Average velocity and u' is random velocity

The Turbulent Advective diffusion equation

- To derive an ADE for turbulence, we substitute the Reynolds decomposition into the normal ADE and analyze the results.

- The Reynolds decomposition for concentration

- $C(x, t) = \bar{C}(x, t) + C'(x, t)$ where $\int C' dt = 0$

- $\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right) - \frac{\partial(uC)}{\partial x}$

- $\frac{\partial(\bar{C}+C')}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial(\bar{C}+C')}{\partial x} \right) - \frac{\partial((\bar{u}+u')(\bar{C}+C'))}{\partial x}$

- $\frac{\partial(\bar{C}+C')}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial(\bar{C}+C')}{\partial x} \right) - \frac{\partial(\bar{u}\bar{C} + \bar{u}C' + u'\bar{C} + u'C')}{\partial x}$

- $\Rightarrow \frac{\partial \bar{C}}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial \bar{C}}{\partial x} \right) - \bar{u} \frac{\partial \bar{C}}{\partial x} - \frac{\partial(\overline{u'C'})}{\partial x}$

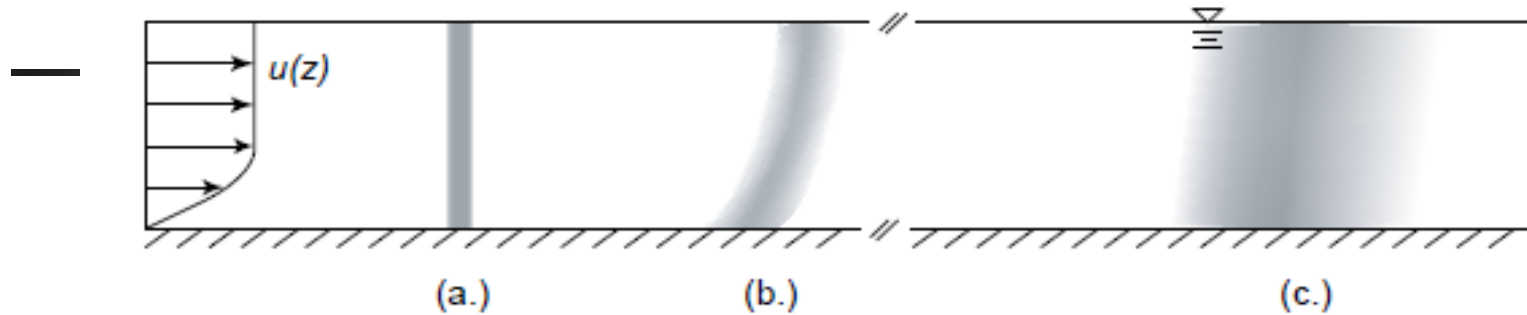
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- To utilize the above equation we require a model for the term $u'C'$. Since this term is of the form uC , it is a mass flux.
 - Since both components of $u'C'$ term are fluctuating, it must be a mass flux associated with the turbulence. Reynolds called it rapid mixing and make an analogy with molecular diffusion.
 - On the average there is no increase in the net advective velocity due to turbulent fluctuations so we model the effect in the diffusional term.

■ $\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left((D_x + e) \frac{\partial c}{\partial x} \right) - u \frac{\partial c}{\partial x}$, Where “e” = turbulent diffusion coefficient.

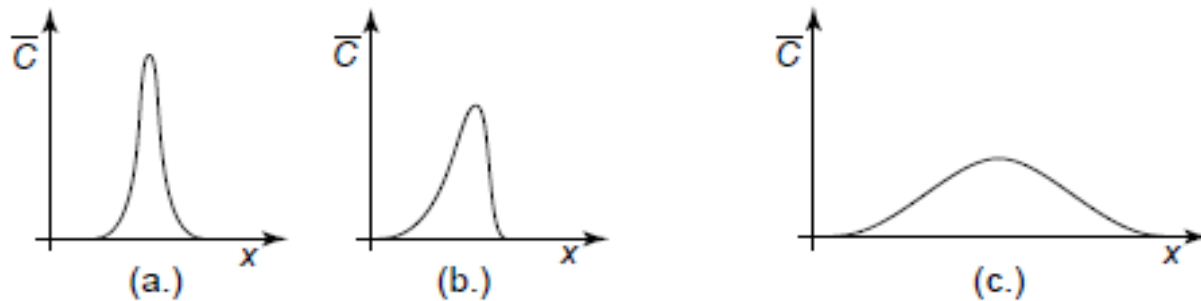
Shear flow dispersion

- If a velocity profile exists and if there is molecular or turbulent diffusion we get shear flow dispersion. Shear flow dispersion occurs even under laminar flow conditions.
- Shear flow dispersion is a result of the interaction of turbulent & molecular diffusion and shear velocity.
- As shown below. The differential velocity at each depth, coupled with molecular and/or turbulent diffusion and a concentration profile (of the material being mixed) transverse to this velocity results in shear flow dispersion (mixing in the direction of flow).

Side view of river:



Depth-average concentration distributions:



- Schematic showing the process of longitudinal dispersion. Tracer is injected uniformly at (a) and stretched by the shear profile at (b). At (c) vertical diffusion has homogenized the vertical gradients and a depth-averaged Gaussian distribution is expected in the concentration profiles.

Shear flow dispersion

- Once again this type of diffusion is included in the diffusive term of the advective diffusion equation. So the resulting advective-diffusion equation finally looks like:

$$\blacksquare \frac{\partial C}{\partial t} = (D_x + e + E_L) \frac{\partial^2 C}{\partial x^2} - u \frac{\partial C}{\partial x}$$

- Where E_L is the longitudinal dispersion coefficient (i.e., dispersion in the direction of flow).
- All types of diffusion and dispersion are often combined into an overall diffusion coefficient call D_d because it is difficult to separate the individual contributions of each.
- Where $D_d = D + e + E_L$ In many reactors longitudinal dispersion dominates so D_d is approximated by E_L .

$$\blacksquare \frac{\partial C}{\partial t} = D_d \frac{\partial^2 C}{\partial x^2} - u \frac{\partial C}{\partial x}$$

Environmental Reactors characteristics

- Mass transfer in reactors (Surface and Sub surface water) results from *advection* (bulk fluid transport) and *diffusion* (*mostly dispersion*)
- Mixing level is quantified by the diffusion (dispersion) coefficient, D_d [cm^2/sec , or similar units]).
- The relative importance of advective transport vs. dispersion is characterized by a dimensionless parameter called the Peclet Number (Pe), defined as: $Pe = \frac{Lu}{D_d}$
- Where:
 - L = Characteristic length (usually reactor length) [L];
 - u = Advective velocity [L/T];
 - D_d = Dispersion coefficient [L^2/T].

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- Mixing levels give rise to three categories of reactors.
 - Plug-flow (PF) represents no axial dispersion,
 - $P_e = \infty$
 - Complete-mix flow (CMF) with infinite dispersion,
 - $P_e = 0$.
 - Flow with dispersion (FD),
 - $0 < P_e < \infty$

Physical, Chemical and Biological Transformations

- Systems where the mass of a given species of interest is not conserving is the focus of this section.
- Processes that remove mass can be physical, chemical or biological. Since the total mass of the system must be conserved, these processes generally change the species of interest into another species; thus, we will call these processes transformation.
- Transformation is defined as production (or loss) of a given species of interest through physical, chemical, or biological processes.
- When no transformation occurs, the system is said to be **conservative**, and we represent this characteristic mathematically with the conservation of mass equation:

$$\blacksquare \frac{dM_i}{dt} = 0, \text{ where } M_i \text{ is the total mass of species } i.$$

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- When transformation does occur, the system is called **reactive**, and, for a given species of interest, the system is no longer conservative. We represent this characteristic mathematically as

$$\blacksquare \frac{dM_i}{dt} = S_i, \text{ where } S_i \text{ is a source or sink term.}$$

- For reactive systems, we must supply reaction equations that describe the production or loss of the species of interest.
- Since the total system mass must be conserved, these reactions are often represented by a system of transformation equations.
- Transformation are categorized as either homo- or hetero-geneous.
- Homogeneous reactions occur everywhere in the control volume; hence, they are represented as a source or sink term in the governing differential equation.

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- By contrast, heterogeneous reactions occur only at control volume boundaries. hence, they are specified by source or sink boundary conditions constraining the governing differential equation.
 - Some reactions have properties of both homo- and hetero-geneous reactions. A reaction that occurs on the surface of suspended sediment particles. Because the reaction occurs only at the sediment/water interface, the reaction is heterogeneous. But, because the sediment is suspended throughout the water column, the effect of the reaction is homogeneous in nature.
 - Models that represent the reaction through boundary conditions (i.e. they treat the reaction as heterogeneous) are sometimes called **two-phase, or multi-phase**, models.
 - Models that simplify the reaction to treat it as a homogeneous reaction are called **single-phase, or mixture**, models. Analytical solutions often possible for the single-phase approach.

Incorporating transformation with the ADE

- **Homogeneous reactions:** add a new term to the ADE because they occur everywhere within REV; hence, they provide another flux to our law of conservation of mass.

$$\blacksquare \frac{\partial C}{\partial t} + u \frac{\partial C}{\partial x} = D_d \frac{\partial^2 C}{\partial x^2} \pm R$$

- where R is a source or sink reaction term per unit volume of REV
- **Heterogeneous reactions:** occur only at the boundaries; hence, they provide new flux boundary conditions as constraints on the ADE. Examples include corrosion, where there is an oxygen sink at the boundary

$$\blacksquare \frac{\partial C}{\partial t} + u \frac{\partial C}{\partial x} = D_d \frac{\partial^2 C}{\partial x^2} \pm J_n$$

- where J_n is a source or sink reaction term per unit surface area of REV

Boundary Exchange: (heterogeneous reactions)

- The two major boundary types in environmental fluid mechanics are the **air-water** and **Solid-water** interfaces.
- The processes at both boundaries are very similar.
- Examples at the air-water interface: chemicals present in both phases (the air and the water), such as O_2 and CO_2 , as well as volatile chemicals that off-gas from the water into the atmosphere, where the concentration is negligible, such as mercuric compounds (e.g. $(CH_3)_2Hg$), chlorinated hydrocarbons (e.g. CH_2Cl), and other organic compounds.
- Examples at the solid-water interface include metals, salts, nutrients, and organic compounds.

Chemical distribution among phases

- One medium may contain different phases. (liquid, gas, solid)
 - Atmosphere contains gas, water, and solids.
 - Surface water contains gas bubbles and particulates.
 - Aquifer contains air, water and solid materials
- Pollutants become distributed between different phases in each medium.
- Solids can be suspended in water or air and
- Liquids can have a partial pressure in air (in the headspace above the aqueous solution).
- Also chemicals can be soluble to some extent in an aqueous solution, with the remainder in a solid state.

Partitioning between phases

- Potentially, chemical agents in the environment can become distributed throughout the gas phase (air), liquid phase (aqueous environments and non-aqueous spillages) and solid phase.
- A non-aqueous phase liquid (NAPL) does not mix freely with water and floats on the surface or may be a submerged bolus depending on density.
- The important solid phase components can be taken to include not only macroscopic surfaces, but also particulate matter suspended in air and water. The microscopic solids are often the more significant of the two; especially during clean-up or decontamination operations.
- Even in the subsurface environment it may be necessary to consider partitioning of some contaminants between soil particles, water and trapped air.

Solubility and Vapor Pressure

- Aqueous solubility is the concentration of a chemical dissolved in water when that water is both in contact and at equilibrium with the pure chemical. Aqueous solubility is temperature dependent, but does not vary greatly over typical environmental temperatures.
- For example, TCE (trichloroethene) dissolves in water until an aqueous concentration of about 1000 mg/L is reached.
- Vapor pressure is defined as the partial pressure of a chemical in a gas phase that is in equilibrium with the pure liquid or solid chemical. Temperature is very important when determining vapor pressure. The ideal gas law is used to convert the partial pressure to the moles of vapor per unit volume:

■ $\frac{n}{V} = \frac{P}{RT}$, Where n/V is the number of moles of the chemical per unit volume, P is the partial pressure, T is the absolute temperature, and R is the gas constant: (0.082 liter-atm)/(mol-K).

Henry's Law Constants

- A partition coefficient describes how a chemical distributes itself between two different phases. The Henry's Law constant, H (or KH), is a partition coefficient defined as the ratio of a chemical's concentration in air to its concentration in water at equilibrium.
- H can be estimated for a chemical by dividing its vapor pressure by its aqueous solubility at the same temperature.
- H generally increases with increasing temperature (vapor pressure changes more rapidly than aqueous solubility with temperature).
- H can be dimensionless (using the same concentration units for the water and air phases), in dimensionless forms, such as atm-Lit/mol or atm-m³/mol. Can be converted:

$$\begin{aligned} \blacksquare H &= \frac{\text{mol chemical/liter air}}{\text{mol chemical/liter water}} \times R \left(\frac{\text{Liter air} \times \text{atm chemical}}{\text{mol chemical} \times K} \right) \times \\ T(K) &= \frac{\text{atm chemical}}{\text{mol chemical/liter water}} = \frac{\text{atm liter}}{\text{mol}} \end{aligned}$$

Adsorbption

- **Adsorption**, the binding of molecules or particles to a surface.
- **Absorption**, the filling of pores in a solid.
- Process of adsorption involves separation of a substance from one phase accompanied by its accumulation or concentration at the surface of another.
- The adsorbing phase is the **adsorbent**, and the material adsorbed at the surface of that phase is the **adsorbate**.
- Adsorption is a term which is completely different from Absorption .While absorption means uniform distribution of the substance throughout the bulk, adsorption essentially happens at the surface of the substance.
- When both Adsorption and Absorption processes take place simultaneously, the process is called **sorption**.

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- Physical adsorption is caused mainly by van der Waals forces and electrostatic forces between adsorbate molecules and the atoms which compose the adsorbent surface.
 - Adsorbents are characterized by surface properties such as surface area and polarity:

1. Surface area:

A large specific surface area is preferable for providing large adsorption capacity, but the creation of a large internal surface area in a limited volume inevitably gives rise to large numbers of small sized pores between adsorption surfaces.

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- The size of the micropores determines the accessibility of adsorbate molecules to the internal adsorption surface, so the pore size distribution of micropores is another important property for characterizing adsorptivity of adsorbents.
 - **2. Surface polarity**
 - Surface polarity corresponds to affinity with polar substances such as water or alcohols. Polar adsorbents are thus called “**hydrophillic**”.
 - On the other hand, nonpolar adsorbents are generally “**hydrophobic**”. These adsorbents have more affinity with oil or hydrocarbons than water.

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- Depending on the **nature of attractive forces** existing between the adsorbate and adsorbent, adsorption can be classified as:
 - **Physical adsorption:** the forces of attraction between the molecules of the adsorbate and the adsorbent are of the weak **van der Waals'** type. Since the forces of attraction are weak, the process of physisorption can be easily reversed by heating or decreasing the pressure of the adsorbate (as in the case of gases).
 - **Chemical adsorption (Chemisorption):** the forces of attraction between the adsorbate and the adsorbent are very strong; the molecules of adsorbate form chemical bonds with the molecules of the adsorbent present in the surface.

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- Sorption isotherms (conducted at a constant temperature) are therefore used to directly measure the partitioning between water and solids.
 - Laboratory data usually fitted to the Freundlich isotherm:
 - $C_{sorb} = K_f (C_w)^n$
 - C_{sorb} is the concentration of the sorbed chemical [M/M];
 - K_f is the Freundlich constant
 - C_w is the concentration of the dissolved chemical [M/L³]
 - n reflects non-linearity:

Factors Influencing Adsorption

1. **Surface Area:** The extent of adsorption is proportional to specific area. Specific area can be defined as that portion of the total area that is available for adsorption.
2. **Nature of the Adsorbate:** Adsorption of a solute is inversely proportional to its solubility in the solvent. The greater the solubility, the stronger the solute-solvent bond and the smaller the extent of adsorption.
 - In general, the solubility of any organic compound in water decreases with increasing chain length, because the compound becomes more hydrocarbon-like as the number of carbon atoms becomes greater .
 - Adsorption of aliphatic series of organic acids increases in the order formic-acetic-propionic-butyric, whereas the order is reversed for adsorption from toluene.

3. Molecular sizes: If the rate is controlled by intraparticle transport, the reaction generally will proceed more rapidly the smaller the adsorbate molecule, within a given class of compound.

4. Charge (Ionic species): As long as the compounds are structurally simple, adsorption is at minimum for the charged species and at a maximum for the neutral species.

- Decreasing adsorption with increasing ionization has been observed for many organic acids. Adsorption of propionic acid on carbon decreases markedly with increasing pH to a minimum in the range pH 3.5 to 5.5 (succinic acid to a min. in the range pH 4.0 and 7.0, caproic acid between pH 4.8 and 7.5).

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- 5. pH:** Because hydrogen and hydroxide ions are adsorbed quite strongly, the adsorption of other ions is influenced by the pH of the solution. In general, adsorption of typical organic pollutant from water is increased with decreasing pH.
- 6. Temperature:** Adsorption reactions are normally exothermic, thus the extent of adsorption generally increases with decreasing temperature.
- 7. Adsorption of Mixed Solutes:** The degree of mutual inhibition of competing adsorbates should be related to the relative sizes of the molecules being adsorbed, to the relative adsorptive affinities, and to the relative concentrations of solutes.

8. Nature of the Adsorbent: The physicochemical nature of the adsorbent can have profound effects on both rate and capacity for adsorption. Commercial carbons can be prepared from a variety of raw materials, including wood, lignite, coal, petroleum residues, and nut shells.